

### A New Iodine Compound: I-OH<sub>2</sub>

WHEN the pH of an I<sub>3</sub><sup>-</sup> solution, approximately one-tenth molar in iodide, is raised to about 12, part of the I<sub>3</sub><sup>-</sup> initially present disappears immediately, and the remainder decomposes slowly, at a measurable rate, due to production of iodate (Fig. 1).

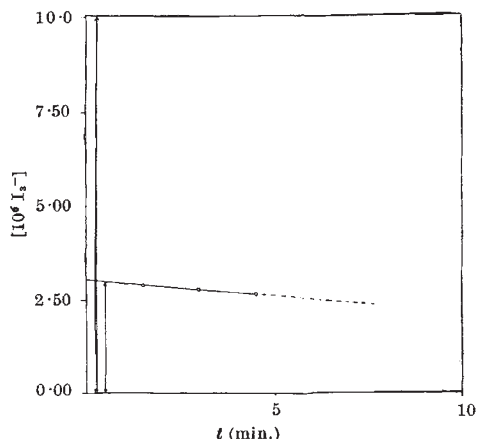
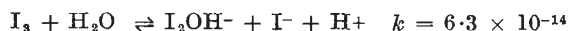
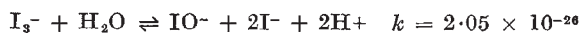


Fig. 1. Disappearance of I<sub>3</sub><sup>-</sup> with time. Long arrow, initial iodine concentration; short arrow, initial I<sub>3</sub><sup>-</sup> concentration. [I<sup>-</sup>], 2.00 × 10<sup>-1</sup> M; [H<sup>+</sup>], 5.35 × 10<sup>-13</sup> M

We have studied quantitatively the instantaneous consumption of I<sub>3</sub><sup>-</sup>, the light absorption of this substance, determined<sup>1</sup> at 350 mμ after alkalization, being extrapolated to zero time. The study was performed in the concentration ranges 8 × 10<sup>-3</sup> < [I<sup>-</sup>] < 6 × 10<sup>-1</sup>, 1 × 10<sup>-13</sup> < [H<sup>+</sup>] < 2.5 × 10<sup>-12</sup> and 5 × 10<sup>-5</sup> < [initial iodine] < 5 × 10<sup>-4</sup> (ionic strength, 0.60; temperature, 25.0° C.), in such conditions that the concentrations of I<sub>2</sub>, IOH and I<sup>+</sup> may be neglected. Results have shown that the total effect is linked with the occurrence of two reactions, one producing IO<sup>-</sup>, the other the new compound I<sub>2</sub>OH<sup>-</sup>:



In the past, the determination of equilibrium constants of reactions involving IO<sup>-</sup>,<sup>2,3</sup> and IOH<sup>1,4,5</sup> has often led to contradictory values. Taking the presence of I<sub>2</sub>OH<sup>-</sup> in these systems into account explains this anomalous behaviour, and removes the contradictions.

The relative amounts of I<sub>2</sub>OH<sup>-</sup> and IOH depend only on the concentration of iodide:

$$\frac{[I_2OH^-]}{[IOH]} = 1.0 \times 10^3 [I^-]$$

The I<sub>2</sub>OH<sup>-</sup> concentration consequently exceeds that of hypiodous acid when [I<sup>-</sup>] > 10<sup>-2</sup>.

I<sub>2</sub>OH<sup>-</sup> may be considered as similar to I<sub>2</sub>Cl<sup>-</sup>, I<sub>2</sub>Br<sup>-</sup> and I<sub>3</sub><sup>-</sup>. It seems probable that it is involved in the mechanism of iodine reactions.

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### Hydrated Glasses

It has been found that in silicate and aluminosilicate glasses the vitreous network of linked groups of tetrahedrally arranged oxygen atoms responds to differences of composition by dilation or by contraction<sup>1,2</sup>. This effect is of especial interest in the case of natural glasses, where the water content varies greatly.

Data relating to 132 such glasses have been studied, including 82 of acid composition. Of the latter, 40 rhyolitic and rhyo-dacitic obsidians constitute a well-defined group in which the water content averages about 0.3 per cent by weight, reaching a maximum of 1 per cent. Consideration of the various structural alternatives in the light of the observed physical properties and thermal behaviour suggests that the water is present in these rocks in the form of hydroxyl ions combined as randomly distributed single SiO<sub>3</sub>(OH) or AlO<sub>3</sub>(OH) groups. This water was acquired while the material was molten, and the proposed structure reflects the low-pressure environment in which cooling occurred.

The remaining 42 acid glasses include intrusive and extrusive pitchstones, a fused grit, a fused granodiorite, perlites and glasses separated from the mesostasis of tholeiitic rocks. Their water content ranges from 2 to nearly 10 per cent. The specific gravity data show that the number of glass-forming ions in unit volume is subject to a linear decrease as the water content increases, the total oxygen content of that volume remaining comparatively constant. As compared with the obsidians, the oxygen is packed more tightly to the extent of about 4 per cent. It is postulated that the structural factor responsible for the closer oxygen packing is five-fold co-ordination of the aluminium. Six-fold co-ordination seems to be precluded.

The glasses of this second group are diverse as to origin and history. Certain of them congealed from a hydrous melt. Under the moderately high pressures attending the intrusion of such a melt into upper crustal rocks, it is believed that groupings such as AlO<sub>4</sub>(OH) are formed. The association of the hydroxyl with the AlO<sub>4</sub> group is a passive one, the (OH) forming part of an adjacent tetrahedral cluster.

The structures of acid glasses hydrated after solidification also involve a similar passive co-operation in some instances. Two general types of mechanism are envisaged:

(a) At low temperatures, water penetrates into the expansible three-dimensional network, being held by long hydrogen bonds or in zeolite fashion. Dissociation of water molecules is associated with the rupture of bonds between glass-forming or other cations and oxygen with the production of contiguous hydroxyl pairs. Minor positional adjustments ensue, raising the effective co-ordination number of aluminium. The resultant shrinkage generates stress that may aid the propagation of the reaction and lead to the eventual development of perlitic cracking. This mechanical feature is thus developed only in glasses originally possessing 4-co-ordinated aluminium.

(b) At higher sub-magmatic temperatures, water dissociates upon entry, and a process that may be described as reconstructive cross-linkage brings into being pairs of hydroxyl ions, the individual ions of each pair being near each other but not in contact. Again, the aluminium assumes a five-fold co-ordination.